PREPARATION OF HIDE COLLAGEN FOR FOOD*

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ABSTRACT

Present outlets for hide collagen are threatened by substitutes for leather, gelatin, and glue. Development of alternate uses is required to maintain a profitable market for hides, while a shortage of food protein is forecast. Food use of collagen requires meat inspection authority approval.

Limed splits from fresh hides are delimed, given a light pickle, and washed well in a stainless steel drum to produce a palatable and bacteriologically acceptable collagen. The pH of the splits is in the isoelectric range; ash is about 0.5 percent, and the dry solids about 30 percent. When granulated, the product has very little flavor or odor. Processing time is about eight hours.

Rat feeding experiments show dried ground collagen to be completely digestible. It is an incomplete protein nutritionally but is found to have an energy value 86 percent that of casein.

INTRODUCTION

Food use of collagen from cattlehide is a concept given impetus from the fact that the two billion pounds now going into leather, gelatin, and glue are threatened by commercial production of substitutes. Since the hide represents seven to eight percent of the live animal weight (1), its value is of importance to the cattleman and packer. In addition, tanners are finding a shrinking demand for byproduct fleshings, trimmings, and splits, which is made more serious by antipollution and dumping regulations.

Not all hides can be used for food purposes. Collagen must come from inspected slaughter and identity with acceptable carcasses must be established for all hides intended for food use. Packers have stated that this is not a serious problem.

Limed flesh splits from any fresh cattlehide are satisfactory for *experimental* work. Collagen produced has been acceptable bacteriologically and has no of-

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fensive flavor or odor if processed quickly and carefully in suitable equipment. Limed split appears to be sterile because of the high pH. Fat is a source of odors, either from staling, oxidation, or entrapment of odors from equipment, and is not easily removed.

EXPERIMENTAL

Limed flesh splits were purchased from a nearby tannery where fresh stock, obtained from local slaughterhouses, is processed separately from cured stock. Before this system was established some disappointing results were experienced, in that collagen produced was seldom palatable. We further attempted to avoid stock that had been held over a week end or holiday and to use only material that had been promptly limed after slaughter and was relatively clean and free of particulate matter. Usually the splits were from well-fleshed hides. Splits from whole hides were available and were useful as sides when control for an experimental change was required. Weights of whole splits were between 22 and 44 lbs. each.

Splits were sided and 37 to 250 lbs. were placed in a 24″ x 60″ (internal) wooden drum run at 8–12 r.p.m. and washed for 30 minutes in cold running water. This removed superficial lime, loose fiber, and a part of any clinging particulate matter, such as wood flour or sawdust used in splitting. (A soluble salt, such as granulated sodium chloride, would be preferred as a traction assist in splitting for edible collagen.)

After washing, the splits were drained in the drum through the wash door for about ten minutes. The drum was opened and five percent ammonium chloride on the limed split weight was added dry. The drum was closed with a solid door and run for about ten minutes, when a small float had developed. One percent lactic acid (Practical or USP 85 percent) (v/w) was added and drumming was continued. During the first hour three percent or one percent feeds of six percent (v/v) sulfuric acid were made to maintain the liquor well below pH 4. In the high ionic strength developed by ammonium chloride and calcium chloride, a low pH did not swell the splits. Changes in pH in the hide and liquor during drum processing are shown in Figure 1. A pink streak remained in heavy parts of the splits when a cut surface was tested with phenolphthalein. Additionally, at this time the average pH of a heavy area was determined by cutting a one- to two-gram sample at least an inch from an edge, disintegrating the sample in 200 ml. distilled water in a Waring Blendor‡ for one minute, and taking the pH by meter. Thinner areas of the split equilibrate with the liquor much more rapidly, and it is reasonable to assume that the average pH is between that of the liquor and that of the fibered thick section. The difference in these values is significant in assessing the completeness of acidification. The splits were in

‡Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

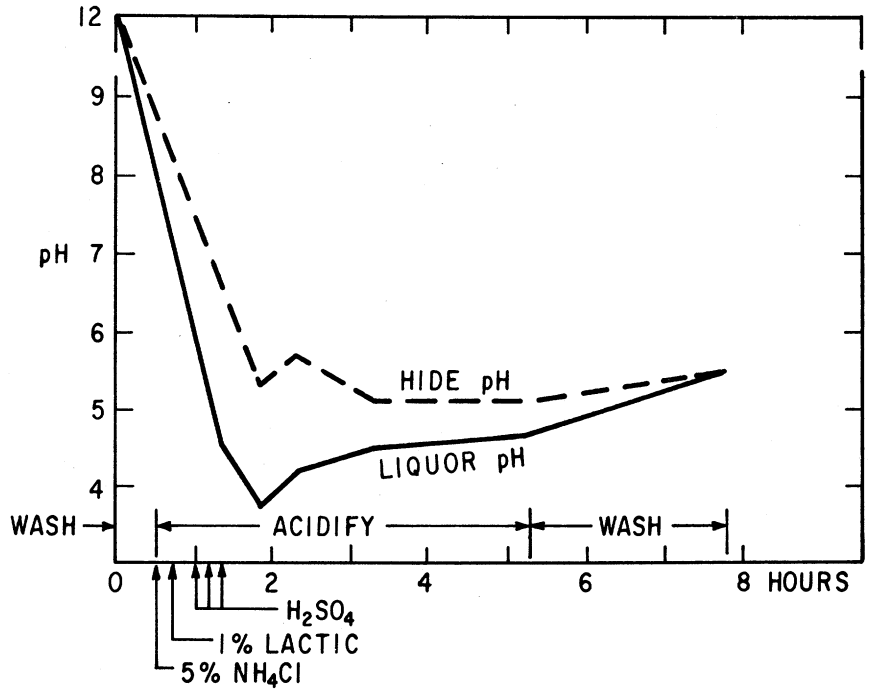

FIGURE 1.—Hide pH is measured by cutting a 1–2 gram block at least an inch from an edge, disintegrating the sample in 200 ml. distilled water in a blender for one minute, and taking the pH by meter. Liquor pH is measured without dilution with a glass electrode. Feeds of ammonium chloride and lactic acid (85 percent) are percent of limed weight. Feeds of sulfuric acid (six percent) are made as required to adjust pH to <4. Usual acid requirements are shown in Table II.

satisfactory equilibrium with the liquor when the two values were about one half pH unit apart.

Neutralization and acidification were usually completed to this point in 2.5 to three hours. Washing was then begun in a slow flow of cold water and continued for 2.5 hours. Buffer was removed by the wash and the final pH of the collagen was found to be shifted toward the pH of the water. After washing, the splits were horsed for an hour and refrigerated overnight. Collagen processed in this way had an average pH between 4.5 and 6.8 and an ash below 0.5 percent.

Relationships between liquor pH, Waring Blendor (hide) pH, and pH of the washed splits in several lots are shown in Table I.

Liquor pH was measured after all acid had been added, just prior to washing. Waring Blendor pH of a thick sample was measured at the same time and represents the highest average pH in the split. During washing, buffer was removed from the split and the average pH rose markedly above that of the buffer and slightly above the Waring Blendor pH. The wash water had a pH of 6–7.

TABLE I

RELATIONSHIPS BETWEEN LIQUOR pH, WARING BLENDOR (HIDE) pH, AND pH OF THE WASHED SPLITS

Lot	Final Liquor pH	Waring Blendor pH	Washed Splits pH
F17	4.2	4.7	4.5
F18	3.9	4.3	4.7
F20	4.3	5.0	5.4
F21	4.7	5.1	5.4
F28D	4.7	6.8	6.8 (0.5 hr. wash)

Acid requirements are influenced by pretreatment and final pH of the splits. Results in Table II show variations experienced in several experimental lots. In cases where pH of the splits had been reduced below 4.2, washing reduced ionic strength, allowing the collagen to swell as in lots F16 and 23, which prevented further efficient washing. Lots 22 and 23 were from the same tannery lot of hides.

TABLE II

ACID REQUIREMENTS IN PROCESSING SEVERAL LOTS OF SPLITS

Lot	Lactic Acid* (%)	H_2SO_4 (Conc.) (ml./lb.)	Washed pH
F16	2	2.85	3.9
F18	1	2.90	4.7
22	1	3.87	4.8
23	1	3.88	3.9
26	1	2.32	4.8

*In each case five percent ammonium chloride on the limed split weight was added.

The refrigerated splits were cut in successive operations while wet or after freezing, and yielded a maximum particle dimension of about 1/8 inch. Samples were taken from this well-mixed mass to determine final pH by addition of a small amount of distilled water to wet the electrodes. Fat was measured by acetone extraction in a Soxhlet. Solids were determined by heating a 10–20 gram aliquot at 105°C. overnight.

Modification of the process described above was controlled by using sides from the same splits for two lots. Results of a few of these experiments follow:

(1) Phosphoric acid was added to the delimed hide to reach a washed pH of 6–7. Ash of more than five percent resulted after washing and granulating.

(2) Non-ionic detergent was added to emulsify and reduce fat at body temperature and at room temperature without achieving adequate fat removal. Less than 50 percent was removed.

(3) The same detergent was added at 132°F. and removed about 90 percent of the fat. Splits were obviously shrunk and denatured. We have not yet determined whether shrinking damages collagen for food use, or that shrinkage is essential for good fat removal without solvent.

(4) Several attempts were made to remove sawdust used for traction in splitting. Washing with strong swelling acids, weak swelling acids, or caustic soda was unsuccessful. The actual percent of split weight represented by sawdust is small, but the aesthetic effect and the contamination from this source can be considerable.

(5) Processing in a wood drum resulted in splits with unacceptably high bacterial contamination, although the starting limed splits were free of bacteria. Sides from one lot of limed splits were processed simultaneously in a stainless steel and a wood drum and again sampled for bacterial examination. Results shown in Table III indicate the adverse effect of the wooden drum. The data also suggest that washing, even with potable water, was responsible for mild contamination. The Coliforms found were from the tap water and probably not pathogenic. Salmonella, a contaminant of recent interest and concern in foods, has not been found in the few splits tested. However, collagen was shown to be a poor growth medium when inoculated with salmonellae experimentally.

TABLE III

BACTERIOLOGICAL STUDY OF LIMED SPLITS BEFORE AND AFTER PROCESSING IN WOOD OR STAINLESS STEEL DRUMS

	F28 Limed	F28A Stainless Drum	F28B Wood Drum
Std. Plate Count/g. (27°C.)	NIL	NIL	8500
Coliforms mpn Count/g.	NIL	7.8	33*
Salmonellae	NEG.	NEG.	NEG.
Yeasts & Molds	NIL	NIL	NIL
Std. Plate Count/g. (37°C.)	NIL	NIL	1850

*Too high for food.

DISCUSSION

The processing described is essentially a light pickling to bring the pH of the limed splits to a point in the isoelectric range, followed by prolonged washing to reduce salt content. For some purposes the salts may not be objectionable, either for further processing or for food use, especially if sodium chloride is the salt.

After liming, it is essential to keep the splits clean both bacteriologically and physically. Wooden equipment is apparently not satisfactory bacteriologically. Substitutes for stainless steel may be available and adequate, but we have not tested them.

Collagen is a nutritionally incomplete protein. It contains no tryptophan and is low in methionine. In adult man 80–89 percent of the methionine requirement can be met by cystine, a non-essential amino acid. However, there is no cystine in collagen. This is, of course, why hides and skins can be unhaired without damage to the collagen. In Table IV the two columns at the left show the eight essential amino acids and the human daily dietary requirements for each of them. These values are "safe," about double the minimum requirements (2). The next column shows the essential amino acid levels in purified collagen found by Bowes, Elliott, and Moss (3), expressed as grams per 100 grams (or percent) of the dry protein. If it is assumed that 100 grams of dry collagen is ingested per day as the only source of protein, it would supply only six of the eight essential amino acids at satisfactory levels, as shown in the last column. Life could not be maintained because of the deficiency in two of the amino acids.

The Pharmacology Laboratory of the Department of Agriculture, Western Utilization Research and Development Division at Albany, California, is testing collagen produced as outlined above in rat feeding experiments. For this purpose the processed splits were lyophilized and ground with dry ice to pass a two millimeter screen in the Wiley mill. The fineness of grind was necessary to allow mixture with dry basal diets.

TABLE IV

DIETARY PROTEIN VALUE OF COLLAGEN

Essential Amino Acids	Human Requirement* (Grams/Day)	Grams Amino Acid/100 Grams Collagen†	Excess (+) or Deficiency (−) in Collagen
Tryptophan	0.5	0.0	−0.5
Phenylalanine	2.2	2.4	+0.2
Lysine	1.6	4.0	+2.4
Threonine	1.0	2.3	+1.3
Methionine	2.2‡	1.0	−1.2
Leucine	2.2	3.7	+1.5
Isoleucine	1.4	1.9	+0.5
Valine	1.6	2.5	+0.9
Total	12.7	17.8	+5.1

*Rose, W. C. (2).

†Bowes, J. H., Elliott, R. G., and Moss, J. A. (3).

‡This value was determined with cystine-free diets. In three experiments, the presence of cystine was found to exert a sparing effect of 80 to 89 percent upon the minimal methionine needs of the subjects (2).

Collagen was found to be completely digestible.* It was also found to have 86 percent of the caloric or energy value of casein. Its Protein Efficiency Ratio (P.E.R.), compared to casein as a standard, is low. The P.E.R. is the weight gain in test animals divided by the weight of test protein consumed. A deficiency in one or more essential amino acids will result in low weight gain, and the absence of even one essential amino acid in the protein results in a loss of weight by the animal. The amino acids that are low or missing in collagen can be supplied by many other foods, and mixtures of these with collagen could constitute a product of well-balanced protein and caloric value.

Preparation of collagen from lime splits has made a palatable, digestible product which, with certain precautions, can be made edible for humans. With the change to central beamhouse operation under way it is reasonable to expect commercial production of potentially food grade collagen in large volume. Future work can be directed toward methods for using collagen in foods.

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DISCUSSION

MR. GROTA: Thank you very much for this interesting paper. The discussion leader will be Dr. Shu-Tung Tu of the Union Carbide Corporation.

DR. TU: This work certainly established the desirability of using collagen in food. Dietary consumption of pigskin collagen in the Orient further supports these results. This implies in the near future, at least, we can advantageously use hide collagen in food if we could not use it to make leather as a result of the competition from synthetics. Dr. R. Lollar estimated a future commercial market price for food-grade fibrous hide collagen at $1.40–$1.75/lb. When it is used in products such as sausage casing, for which collagen, as a major component, sells at a price of $13/lb., the market can support this price. I hope in further development along this line that hide trimmings and scraps could be the source of the collagen, so that the croupons can be used efficiently in leather production. Such an effort will complement the tanning industry and help to solve some of the pollution problems. Mr. Whitmore and the USDA team should be congratulated for starting such an important and interesting investigation. Mr. Whitmore, do you care to comment on the feasibility of using hide trimmings and scraps as the source of collagen in food?

*Booth, A. N. Personal communication, U. S. Department of Agriculture, 800 Buchanan St., Albany, California 94710.

MR. WHITMORE: As stated in the paper, collagen for food use must come from inspected slaughter. From the point of inspection the hides must be handled under controlled conditions suitable for food processing. It should be possible to produce collagen for food use from the flesh split and leather from the grain split. We have not used full-grain hide scrap in our work.

DR. TU: What is the required fiber length of collagen in a food application?

MR. WHITMORE: Fiber length or the requirement for dispersion to fibers is determined by the end use of the collagen. Collagen in granular form with very few free fibers has interesting effects in food.

DR. TU: If it is not necessary to have fibrous collagen, can we use gelatin?

MR. WHITMORE: Gelatin is rather costly and has not shown the same effects in cooked food as fibrous or granulated collagen. As we all know, gelatin is quite soluble as compared to collagen.

DR. TU: Are there questions from the floor?

MRS. J. TANCOUS (Tanners' Council Research Laboratory): What does the palatable product look like?

MR. WHITMORE: After cutting or fibering, it is a white granule or dough-like mass.

MR. R. BORESEN (Leas and McVitty, Inc.): Why did you choose the pH of 4 to 6 as your standard? Is it because this represents the isoelectric point?

MR. WHITMORE: No. In food use it will be used in or near this range. Also, the splits are easier to work with and process.

DR. L. SELIGSBERGER (U. S. Army Natick Laboratory): What is the volume of water necessary in the washing process? In the face of a threatening water shortage, could it be reduced?

MR. WHITMORE: We may have used too much water for washing in our experiments. If ash or salts are not a problem in further processing, washing can be drastically reduced.

DR. SELIGSBERGER: What was the size of the flesh splits in this study?

MR. WHITMORE: The flesh splits we used were whole, weighing 25 to 45 lbs. each before siding.

DR. TU: I still recall our discussion on collagen utilization with Mr. A. Hirsch years ago. Mr. Hirsch made soup from hide scraps and he tasted it and found it to be delicious. Do you care to comment, Mr. Hirsch?

MR. HIRSCH (Albert Trostel and Sons Company): Yes, it was a hydrolysate from cowhair which could be consumed as a bouillon and which tasted very much like a beef broth.

DR. TU: More questions from the floor? If not, let us thank Mr. Whitmore for this fine piecee of work.

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